Anticlinic Smectic-*C* Surfaces on Smectic-*A* Freely Suspended Liquid-Crystal Films

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Freely suspended liquid-crystal films in the (orthogonal) smectic-*A* phase often have tilted, smectic-*C*–like surfaces. We report experimental evidence of anticlinic ordering of such surfaces in smectic-*A* films of both chiral and racemic TFMHPOBC, materials with both synclinic and anticlinic bulk phases, as well as chiral DOBAMBC, which has only synclinic bulk phases. In the chiral materials, the surfaces can be switched into the synclinic orientation by applying an electric field above a critical value. [S0031-9007(99)08698-6]

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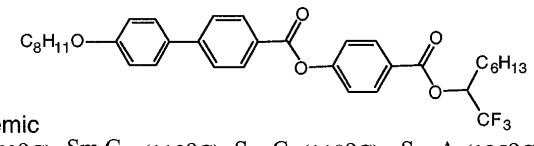
Smectic liquid crystals form stable ultrathin freely suspended films which are quantized in thickness in units of smectic layers [1]. Such films have played a critical role in elucidating the structure and phase behavior of layered liquid crystal materials. Examples of this are the unambiguous confirmation of the layer-by-layer anticlinic ordering of antiferroelectric liquid crystals [2] and the determination of the antiferroelectric ground state of chiral smectics made from achiral bent-core molecules [3]. Care must be taken in drawing conclusions about the bulk properties of liquid crystals from the behavior of films, as the surface layers of the film may be in a phase with higher or lower order than the interior of the film. Indeed, the surface phases may not even exist as bulk phases of the material [4,5]. For the particular case of nominally smectic-*A* (Sm*A*) films, there is typically a temperature range over which the film has smectic-*C* (Sm*C*) surfaces tilted in the same direction and an interior Sm*A* [6]. Recently Andreeva *et al.* reported evidence of SmA^* films adopting *oppositely* tilted (anticlinic) surfaces in the presence of an applied electric field **E** [7]. To explain their observations, they proposed that the field couples to a giant flexoelectric polarization $\mathbf{P}_f$ in the tilt plane of the surface molecules, reorienting the director on the tilt cone into the anticlinic structure. In this Letter, we report that the anticlinic surface structure can in fact be the *ground state* for such films even in the absence of an applied field, and we demonstrate that for chiral materials the surfaces can be driven *synclinic* (tilting in the same direction) by a sufficiently large E. This field-induced change from anticlinic to synclinic ordering, although forbidden in the model proposed by Andreeva *et al.*, can explain the puzzling ellipsometric observations reported recently by Schlauf and Bahr [8].

Freely suspended films of chiral (*R*)-TFMHPOBC and racemic TFMHPOBC were drawn over a 3-mm-radius hole in a glass coverslip in the Sm*A* phase. The molecular structure and phase diagrams are shown in Fig. 1. The exact number of smectic layers, N, was determined by laser reflectivity [9]. The projection of the director, **n**, onto the film surface defines the **c** director, which was visualized using depolarized reflected light microscopy [10,11]. Titanium electrodes evaporated on the glass coverslip were used to apply an electric field **E** in the plane of the film. Laser light (1–3 W) from a multiline argon ion laser was required to image these films because only the surface layers are tilted and their tilt angle is small, resulting in very low overall birefringence.

Initially we studied films in the SmC_A phase. While the chiral material exhibited the previously reported odd-even effect (where films with N odd have transverse ferroelectricity and N even have longitudinal ferroelectricity) [12], as expected the racemic material behaved differently. The **c** director in racemic films with N even still aligned parallel to an external electric field, but in films with N odd there was no response to the field, as is shown in Fig. 2.

At higher temperatures, a distinct phase transition from the chiral anticlinic (antiferroelectric) SmC_A^* phase to the SmA^* phase in chiral TFMHPOBC, and from the Sm*C* to the Sm*A* phase in racemic TFMHPOBC, could be observed in films of all thicknesses. In both the chiral and racemic cases, the Sm*A* films exhibited a nonzero birefringence and **c**-director fluctuations indicative of tilted surfaces. All Sm*A* films were found to have longitudinal polarization at low-field strengths, independent of N. This follows from the observation that the **c** director aligns parallel to **E** [12].



racemic
X (60°C) Sm C_A (110°C) Sm C (118°C) Sm A (125°C) Iso

chiral
X (64°C) Sm C_A^* (116°C) Sm A* (125°C) Iso

FIG. 1. Structure and phase transitions of TFMHPOBC.

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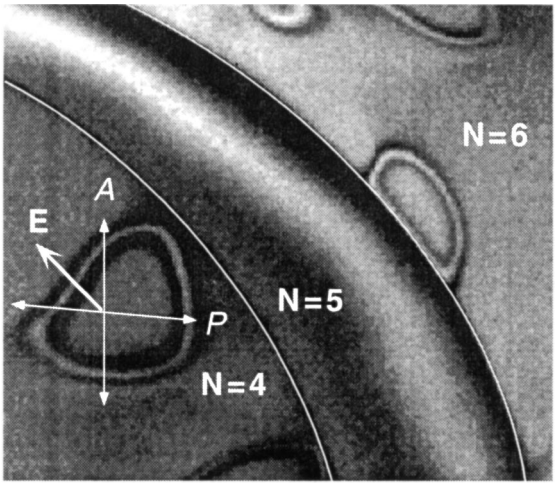

FIG. 2. Racemic TFMHPOBC film with layer steps in the SmC_A phase. In regions with an even number of smectic layers, the **c** director is aligned parallel to the electric field **E**, while in regions with an odd number of layers it is not affected by the field. The horizontal dimension is ~300 μm.

The characteristic behavior of 2π walls which separate and recombine when the sign of **E** changes confirms that this low-field state is ferroelectric [10].

In the chiral material only, we observed that when E is increased above a critical value E_c there is a field-induced transition from net longitudinal to transverse polarization. In an electric field gradient, a sharp boundary separates the low-field state (longitudinal polarization) and the high-field state (transverse polarization) as is shown in Fig. 3. This transition occurs in films of all thicknesses studied ($2 < N < 25$) with E_c ranging from 5 to 15 V/mm. It was found that E_c decreases strongly with both N and temperature T. The high-field state is characterized by the appearance of two sets of *crossing* 2π walls [13], as seen in the white box in Fig. 3, and is metastable after the removal of the field: After the field is removed several seconds pass before a ground state domain nucleates, which then grows to cover the entire film in less than 10 seconds. Figure 4 shows a region of the high-field state shrinking with $E = 0$.

In addition to TFMHPOBC, SmA^* phase films of two other homologs of MHPOBC were found to have longitudinal surface polarization and showed a critical field for the transition to a structure with transverse polarization. Similar effects were also observed in DOBAMBC [14,15], a material with no bulk anticlinic phases.

To explain these observations, we propose that, in the ground state of both chiral and racemic TFMHPOBC films in the SmA phase, the surfaces are tilted anticlinic with respect to one another, as shown in Fig. 5(a). While each surface is optically like a bulk SmC, its polarization density $\mathbf{P}(z)$ is different, for the following reason. In a bulk SmC or SmC^* phase, the longitudinal polarization density within one layer is required to be zero at the C_{2y} symmetry axes at the layer centers and interfaces, and to be antisymmetric about these points. Any polarization density satisfying this symmetry must integrate to zero over every layer. In contrast, the symmetry at the air-liquid crystal interface of freely broken

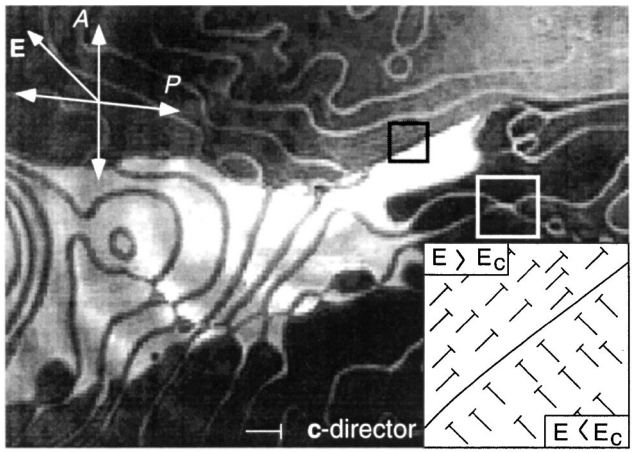

FIG. 3. Freely suspended film of chiral TFMHPOBC in the SmA^* phase with tilted surfaces in an applied field E. The polarizer and analyzer are slightly decrossed, so that regions where the **c** director is aligned parallel to **E** appear white and regions where the **c** director is aligned perpendicular to the field appear black. An electric field gradient with the field larger at the edge of the film than at the center stabilizes two domains. One domain, near the center of the film, is in the low-field state having longitudinal polarization (white), while the second domain is in the high-field state having transverse polarization (black). The white domain grows (shrinks) when E is decreased (increased). The inset shows the **c** director in the black square, which includes a domain boundary. Crossing 2π walls can be seen inside the white square. The white (black) lines in the black (white) domains are 2π walls. The horizontal dimension is ~500 μm.

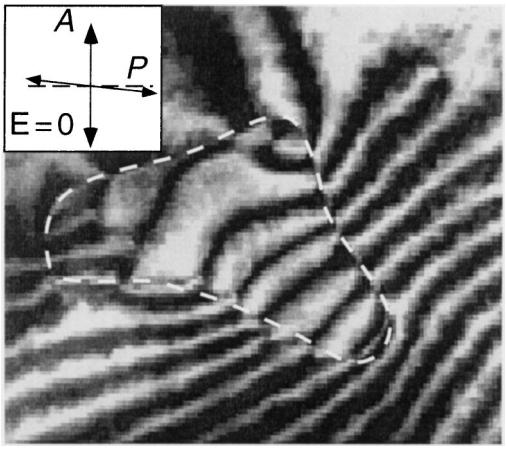

FIG. 4. Metastability of the high-field state. This photomicrograph shows a metastable domain with transverse polarization surrounded by a region in the ground state with longitudinal polarization. Such domains shrink and disappear several seconds after the field is removed. Note that at the domain boundary the black and white brushes reverse, indicating a 90° change in the **c** director orientation across the boundary.

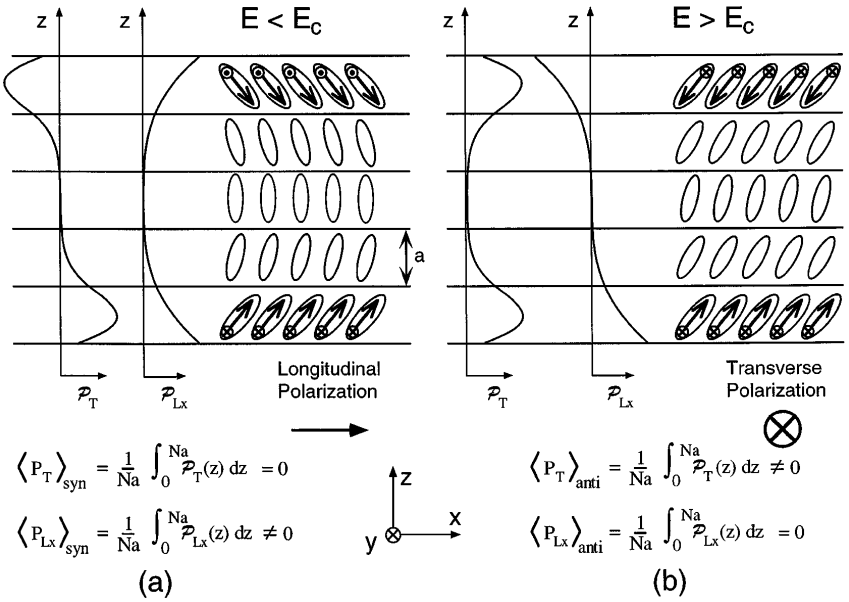

FIG. 5. Model for tilted surfaces in SmA^* films. (a) For $E < E_c$ the surfaces are anticlinic. Polarization densities consistent with the film's symmetry are drawn on the left. The transverse polarization $\mathcal{P}_T$ is required by symmetry to integrate to zero in this case, while the longitudinal polarization $\mathcal{P}_{Lx}$ can integrate to a nonzero value. (b) For $E > E_c$ the surfaces are driven synclinic by the field, the longitudinal surface dipoles cancel, and the integrated polarization is purely transverse. In the integrals N is the number of smectic layers, and a is the thickness of one layer.

suspended films allows local asymmetry of the polarization density near the film surfaces, which means that the surface layers may have an integrated nonzero component of the polarization in the tilt plane, as indicated in Fig. 5(a). If the tilted SmC surfaces of a SmA or SmA^* film are synclinic, the longitudinal polarizations at the bottom and top surfaces cancel identically. For chiral materials the film then has a net transverse polarization, $\langle P_T \rangle_{\rm syn} = (1/Na) \int_0^{Na} \mathcal{P}(z)_T \, dz \neq 0$, as shown in Fig. 5(b), where a is the layer thickness. In a model with tilted surfaces and a SmA interior, the only way for the integrated longitudinal polarization, $\langle P_{Lx} \rangle_{\rm anti} = (1/Na) \int_0^{Na} \mathcal{P}_{Lx}(z) \, dz$, to be nonzero, as we observe, is for the surfaces to be anticlinic. The integrated transverse polarization, $\langle P_T \rangle_{\rm anti}$, in this configuration is zero for both chiral and racemic materials. This model predicts that when the transverse dipoles are on average larger than the in-plane components of the longitudinal dipoles (i.e., $\langle P_T \rangle_{\rm syn} > \langle P_{Lx} \rangle_{\rm anti}$) the surfaces can be switched to be synclinic by a sufficiently large electric field, $E > E_c$. In the synclinic orientation, where the surfaces are effectively decoupled, each surface acts as an independent ferroelectric sheet, and 2π walls can form independently on the top and bottom surfaces of the film and appear to cross each other as is seen experimentally. The observed metastability of the high-field state indicates that both synclinic and anticlinic surface orientations are local energy minima for the film but that the anticlinic arrangement is more stable.

This interpretation is fundamentally different from that of Andreeva *et al.* [7]. In their model, the anticlinic surface structure of Fig. 5(a) is obtained when (i) $P_f > P_T$, (ii) an E field is applied, and (iii) the surfaces are decoupled. If $P_f > P_T$, though, then a transition to the synclinic structure of Fig. 5(b) with increasing field cannot occur. Andreeva *et al.* have not, however, reported any experiments in which the field strength was varied. Of course, P_f may well be greater than P_T (as is the case of the racemate where P_T is identically zero), but this is not necessary for the existence of anticlinic surfaces in general. As the high-field state is synclinic in our experiments, and longitudinal polarization is observed at arbitrarily low-field strengths, we conclude that the $E = 0$ ground state must have anticlinic surfaces. Finally, the existence of a critical field and of a sharp domain boundary between the synclinic and anticlinic structures indicates that the surfaces are in fact coupled together in the ground state structure. Although the experimental observations of Andreeva *et al.* are consistent with ours for $E < E_c$, their model cannot explain our observations when $E > E_c$.

Even if we allow a finite tilt in the interior of the film, a regular layer-by-layer reversal of the tilt direction through the film cannot be the source of the observed anticlinic orientations of the surfaces, as this would result in N-odd films of the chiral material having transverse ferroelectricity, and this is not observed: The ground state polarization is always longitudinal, independent of N. According to the mean-field model of Heinekamp *et al.* [6], the synclinic state shown in Fig. 5(b) is always lower in free energy. In this model, the additional energy associated with anticlinic surfaces scales as $1/N$.

Since we observe experimentally that the anticlinic state becomes more favorable as the films get thinner, the anticlinic orientation must be stabilized by an interaction energy that decreases with decreasing thickness faster than $-1/N$. This interaction, not included in the mean-field model, may be electrostatic in origin.

Surface polarization also explains the existence of longitudinal polarization in the SmC_A (anticlinic) phase of the racemate. Čepič has pointed out that polarization in the tilt plane in N-even films in the SmC_A^* phase could result from incomplete cancellation of P_T contributions from each layer because of the spontaneous partial helixing of the director from the top of the film to the bottom [16]. This model cannot explain our observations, though, because we observe longitudinal polarization even in the case of the racemate, in which the tilt plane of the director is also a mirror symmetry plane, which forbids transverse polarization and does not allow a helix. We believe that the layer-by-layer alternating tilt of the SmC_A phase enforces anticlinic surfaces in N-even films, and the surface polarization has a component in the tilt plane just as in the SmC_A^* films [12].

The recent observations by Schlauf and Bahr [8] of anomalous ellipsometric phase shifts, Δ, in SmA^* films [17] cannot be understood in terms of the conventional synclinic model of tilted surfaces, but are well explained by our anticlinic model. In their experiment, an electric field ($E = 0.8$ V/mm) is applied normal to the plane of incidence of a probe laser. In this geometry, reversing the sign of E causes the director in synclinic surfaces of a SmA^* film to reorient through 180° about the layer normal. These states present different effective refractive indices to the obliquely incident laser beam and result in different optical retardations Δ_+ and Δ_-. In contrast, the prediction from our model with ground state anticlinic surfaces is that, for $E < E_c$, the **c** director aligns parallel to **E** and is normal to the plane of incidence (independent of the sign of **E**) and $\Delta_- - \Delta_+ = 0$. For $E > E_c$, the **c** director aligns in the plane of incidence and $\Delta_- - \Delta_+ \neq 0$. In Schlauf and Bahr's experiments, although E is held constant, N and T are varied. In terms of our model, in thick films (where E_c is very small) E is always above threshold and $\Delta_- - \Delta_+$ is consequently nonzero. For very thin films, E is always below threshold and $\Delta_- - \Delta_+ = 0$. For films with N between these two extremes, there is a temperature range just above the bulk SmC^* to SmA^* transition where $E < E_c$ and $\Delta_- - \Delta_+ = 0$, but, as T increases, E_c decreases, and in a constant applied field E there is a transition to the high-field (synclinic) state where $\Delta_- - \Delta_+$ is nonzero. This model is consistent with what Schlauf and Bahr have described.

In summary, we report the observation of anticlinic tilted surfaces on SmA and SmA^* freely suspended films. Surface polarization combined with this anticlinic tilt results in a spontaneous polarization in the tilt plane (longitudinal polarization) independent of N in both the chiral and racemic materials. If the material is chiral, a transition from longitudinal to transverse polarization can be induced for $E > E_c$, the high-field state having synclinic surfaces. We also report the expected odd-even effect in N for films of the racemate in the anticlinic phase, SmC_A, where N-even films exhibit longitudinal ferroelectricity while N-odd films show no field response. This observation confirms our previously published model for SmC_A^* films [12].

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